

Effects of radiation-induced crosslinking on thermal and mechanical properties of poly(lactic acid) composites reinforced by basalt fiber

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Abstract Poly(lactic acid)/ basalt fiber (PLA/BF) composites were prepared by melt blending with a cross-linking agent, triallyl isocyanurate (TAIC). The thermal and mechanical properties of the composites were investigated through gel fraction, heat deflection temperature (HDT), tensile tests and scanning electron microscopy (SEM). Under certain conditions, the HDT of composites was dramatically increased to 140°C after irradiation. Tensile properties were enhanced as well. Both these improvements were consistent with changes of the fracture morphology. Compatibilization and concomitant enhancement of the interfacial adhesive between the polymer matrix and the inorganic fiber were achieved as seen from SEM photos, as a result of the formation of co-crosslinking and grafting structures at the interface according to the determination of gelation extraction.

Key words Poly(lactic acid), Basalt fiber, Irradiation, Triallyl isocyanurate, HDT

1 Introduction

Poly(lactic acid) (PLA) is a biodegradable polymer produced from renewable plant resources^[1]. It is a linear thermoplastic aliphatic polyester with the glass transition temperature and melting point of 60°C and 175°C, respectively^[2]. PLA shows outstanding biodegradability, biocompatibility, and thermal processing performance. However, as the obvious drawbacks of heat resistance and impact toughness, applications of PLA were limited to the field of medicine, such as surgical suture lines and drug release carriers.

In recent years, there is a tendency to use PLA as a general polymeric material, resulted from the increasing feedstock prices for traditional petroleum derived polymers and the reduction in commercial grade PLA price. Lots of studies have been carried out all over the world, focused on the modification of PLA by various approaches and materials.

As known to us, reinforcement with fibers is usually a powerful technique to improve both the mechanical and thermal properties of polymers. The reinforcement effects of bamboo fiber^[3], sugar beet pulp^[4], wood fiber^[5–8], cellulose fibers^[9–12], hemp fiber^[13–19], and hydroxyapatite fibers^[20,21], etc. on the properties of PLA were investigated. But there were some differences among the final results, due to the differences among matrix resins, various fibers and processing techniques employed. Some researchers^[5,15,21] found the tensile strength of the composites decreased with the fiber content. However, some other studies indicated^[3,6] that the tensile strength firstly increased with the fiber content and then decreased. The literatures^[6,7,18] reported that adding fiber alone did not directly improve the heat deformation temperature of PLA, ascribed to the poor interface adhesion between the fibers and PLA matrix. As the fiber content was more than 15%, the HDT reached 107°C after annealing, because the crystalline played in role of physical cross-linking points^[18].

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As widely investigated, irradiation induced crosslinking is a powerful method in polymer modifications, which was applied to enhanced the thermal properties of PLA^[22–24]. However, high energy rays have rarely been employed in fiber reinforced polymer composites (FRPC). In the present work, we used gamma-irradiation to improve the interfacial adhesion of basalt fiber (BF) reinforced PLA composites. The crosslinking agent, triallyl isocyanurate (TAIC) was added to the composites by melt-blending, which is the most available accelerating agent for the crosslinking of PLA^[25]. The mechanical properties, the gelation fraction, the thermal resistance and the morphology of fracture surface were determined.

2 Experimental

2.1 Materials

PLA (RECODE 101) was supplied by Haizheng biological materials Co. Ltd., China, with the density of 1.25 g/cm³. BF (TEX 7-800) was obtained from Hengdian Group Shanghai Russia Gold Basalt Fiber Co., Ltd., China. TAIC was purchased from Laiyu Chemistry Co. Ltd., China. Chloroform (AR) and absolute alcohol were from Beijing Chemical Plant.

2.2 Sample preparation and irradiation

PLA and BF were dried in vacuum at 80°C for 8 h and in blast air at 120°C for 4 h, respectively. Blending was carried out in a banbury mixer (HAAKE, Germany) with a rotor speed of 50 rpm, at 170°C. The whole processing time was 6 min. The blending ratios of PLA/BF were 90/10, 80/20 and 70/30 by weight, and 1, 2 and 5wt% (to the total weight of PLA and BF) TAIC was added to each composite. Then the samples were prepared by hot pressing with a flat vulcanizing machine (XLB-400×400, China) at 200°C.

The samples were sealed in polyethylene bags filled with nitrogen, and then irradiated at a dosage rate of 3.9 Gy/s in a ⁶⁰Co source at RT. The absorbed doses were 5, 10, 30 and 70 kGy.

2.3 Determination of gel fraction

The samples covered with nickel-mesh were extracted with chloroform in a Soxhlet apparatus at 70°C for 72h.

After washing in alcohol, the extracted samples were dried to a constant weight in blast air at 120°C. The gel fraction was calculated by the formula:

$$G_0 = \frac{W_0 \cdot (1 - B) - (W_0 - W_1)}{W_0 \cdot (1 - B)} \times 100\%$$

where, G_0 is the gel fraction (wt%), and W_0 and W_1 represent the dry weight of samples before and after extraction. B is the content of fiber in the composites.

2.4 Heat deflection temperature (HDT)

A computer-controlled Heat Deformation Vicat Temperature Testing Machine (WKW-300, China) was used to determine the heat deflection temperature. The samples with the size of 10 mm×10 mm×1.2 mm were fixed in a holder and heated from RT with a heating rate of 12°C/6 min in silicon oil medium under a constant load of 1000 g. The humidity is 45%. The measurements were achieved as the deformation quantity reached 1mm according to GB/T1633-2000.

2.5 Mechanical properties

Tensile strength of various samples was tested with an Instron Universal Testing Instrument (INSTRON 1121, USA) at RT. The loading rate was 5 mm/min.

2.6 Scanning electron microscope (SEM)

The specimens were cut from fracture surface of tension samples and coated with a thin layer of gold, then examined with a Scanning Electron Microscope (SEM) (XL 30, USA).

3 Results and discussion

3.1 Gel fraction

The gelation fraction of different PLA/BF composites irradiated at various absorbed doses is shown in Fig.1. It can be seen that gelation was not formed in PLA/BF composites without TAIC as the increasing of absorbed doses. However, for PLA/BF/TAIC composites, the gel content increased significantly after exposure to gamma-rays, which is consistent with Jin's study^[26]. Irradiation played an important role in the crosslinking of composites as well. By and large, in the presence of TAIC, the gel fraction increased obviously in low dosage area, namely 5–10 kGy and

then changed moderately with farther increase of absorbed dose. BF content has little effect on the ultimate amount of networks. In the optimum

conditions, about 60 wt% networks were achieved for the composites blended with 5 wt% TAIC.

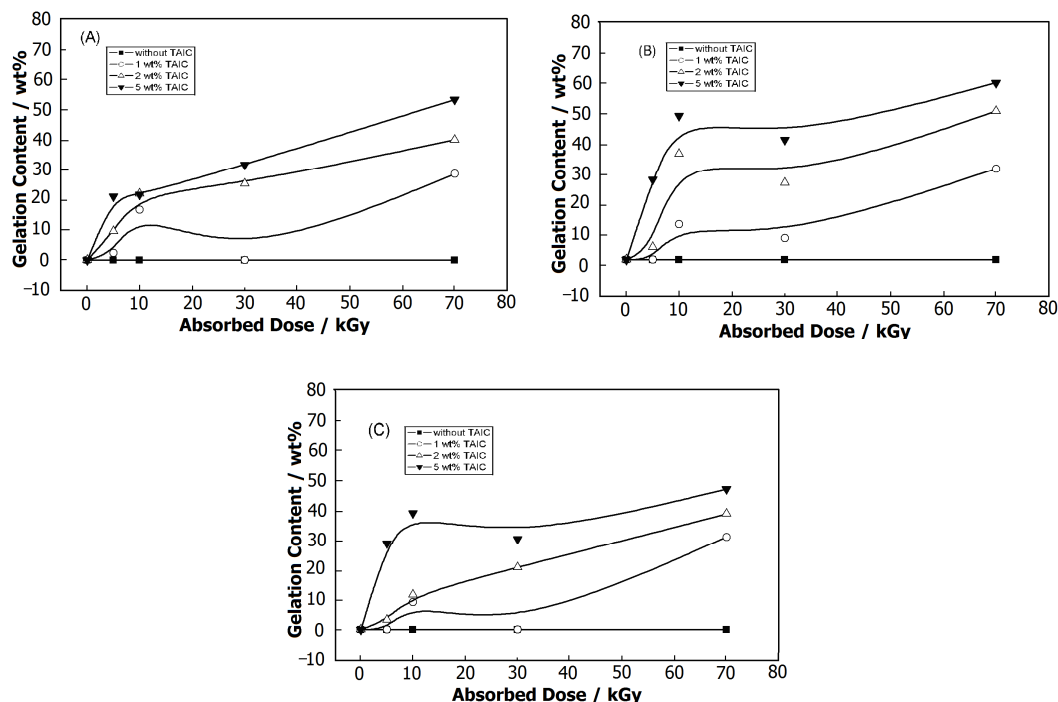


Fig.1 Gelation content of irradiated composites with different amounts of TAIC at various absorbed dose: (A) PLA/BF, 90/10 wt/wt; (B) 80/20; (C) 70/30.

3.2 Heat deflection temperature (HDT)

HDT of PLA/BF composites with various blending ratios after irradiation at 5 kGy have been shown in Fig.2. HDT of PLA/TAIC blends have also been given for contrast. It can be seen that the content of basalt fiber has great impact on the final heat resistance. When the fiber content was less than 20wt%, the HDT of PLA/BF composites were increased by 5–15°C, compared with neat PLA. It kept mostly unchangeable with the increase of TAIC content. As the amount of basalt fiber reached 30wt%, the HDT of PLA/BF binary composite was improved to 85°C after irradiation. As the addition of TAIC, HDT changed slowly at small amount of TAIC, and then dramatically increased to 135°C in the presence of 5wt% TAIC. To take the density into account, the volumetric fraction of basalt fiber was much lower than 30%, due to the much higher density of basalt fiber compared with neat PLA. The heat resistance of PLA can be improved by enhanced irradiation, and appropriate amounts of basalt fiber and TAIC are necessary.

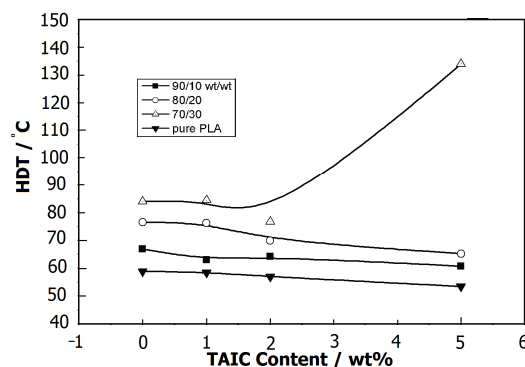


Fig.2 Plot of HDT of different PLA/BF composites with TAIC content at 5 kGy.

The effects of absorbed dose on HDT of PLA/BF/TAIC composites have been shown in Fig.3. The content of TAIC was fixed at 5wt%. Similar to Fig.2, HDT almost remained constant around 65°C with the increase of absorbed dose when the content of basalt fiber was below 20wt%. It also can be found that the HDT of PLA/BF composite (70/30 wt/wt) blended with 5wt% TAIC was significantly enhanced to 135°C after irradiation, even though the gel fraction of bulk PLA in the composites was less than 50wt%. However,

in N. Nagasawa's^[25] and H. Mitomo's^[24] studies 80wt% gelation of PLA was needed to improve the HDT obviously. This difference maybe led by the formation of PLA-g-BF structure at the interphase during enhanced irradiation, and the movements of PLA chains were seriously hindered. The optimum dose was 5–10 kGy, and the further increase of absorbed dose did not lead corresponding improvement of HDT.

3.3 Mechanical properties

Tensile strength of various PLA/BF/TAIC composites has been shown in Fig.4. The property of control samples without TAIC was given as well. It can be observed that the tensile strength of composites without TAIC decreased with absorbed dose on the whole, ascribed to the degradation of PLA chains during the exposure in gamma-rays. The incorporation of small molecules, namely TAIC, enhanced tensile

strength, even though that was not obvious in the low dose area, especially for the composites containing less than 20wt% basalt fiber. As the absorbed dose reached 70 kGy, the tensile strength of composites with TAIC was significantly higher than that of control ones. It may be attributed to adequate amount of networks formed at high dose.

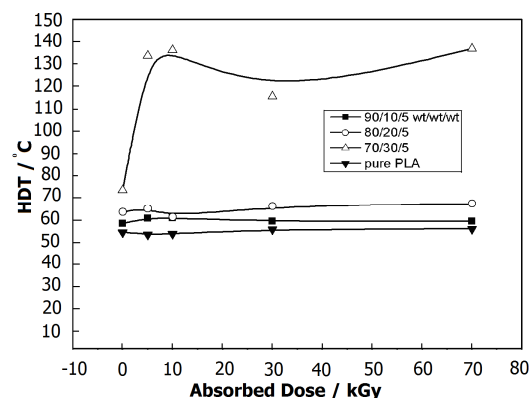


Fig.3 HDT of different PLA/BF/TAIC composites at various absorbed dose.

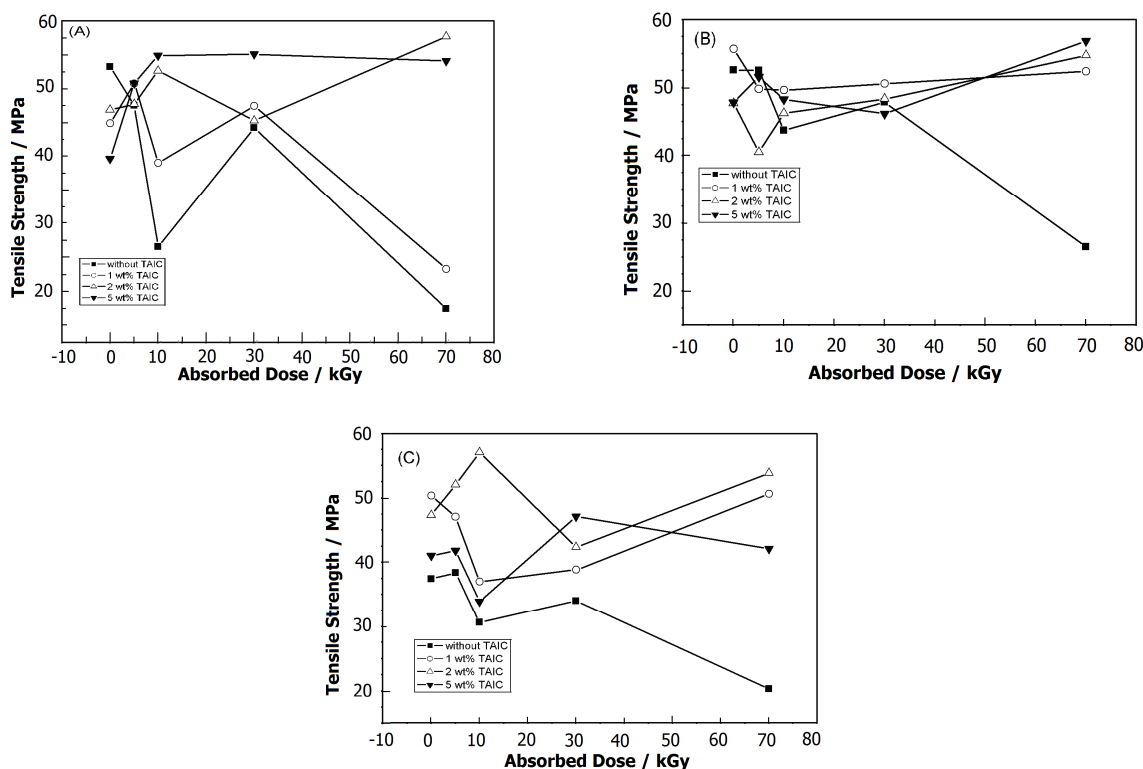


Fig.4 Tensile strength of PLA/BF composites with different content of TAIC at various dose: (A) PLA/BF, 90/10 wt/wt; (B) 80/20; (C) 70/30.

3.4 Mechanism of enhanced radiation crosslinking composite

In the previous papers^[24,27,28], PLA was irradiated by γ

radiation, and H-abstraction occurred predominantly on PLA chains. H. Mitomo indicated that if TAIC molecules coexisted with PLA, the double bonds of allyl groups in TAIC would be broken to form a pair of

radicals $-\text{CH}-\text{CH}_2-$, and a complex structure might be generated between PLA and TAIC molecules^[27].

In the present work it is considered that another crosslinking structure like PLA-g-TAIC-g-BF must form in the composites, besides the network of PLA chains. As is well known, lots of free radicals were formed on PLA chains during irradiation, and these

reactive ones would be combined with TAIC molecules. At the same time, the fibers produced free radicals as well, and these ones would react with the remanent vinyls in the TAIC molecules. Finally, a complex crosslinking structure containing both fibers and PLA segments was achieved at the interface. This reaction process has been shown in Fig.5.

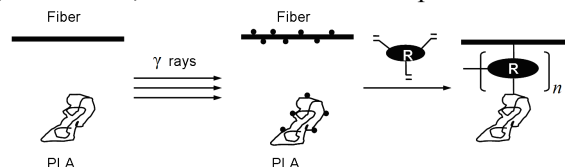


Fig.5 Radiation induce crosslinking mechanism of PLA/fiber composites as TAIC coexistence.

Based on the preceding speculation, it can be concluded that due to the PLA-g-TAIC-g-BF structures at the interface, the restless PLA chains were fixed by rigid fibers at high temperature. These conclusions have already been confirmed by the effectively improved heat resistance. Otherwise, because of this compound at the interface, the necessary amounts of fiber and gel fraction of PLA were reduced to 20 wt% and 50 wt%, respectively.

3.5 SEM

Figure 6 shows the fracture surface of the composites. From the micrographs, it can be observed the surfaces of fibers pulled out from the matrix are very smooth as well as the holes in the matrix, regardless of the change of the fiber content, indicating the weak adhesion between PLA matrix and basalt fiber.

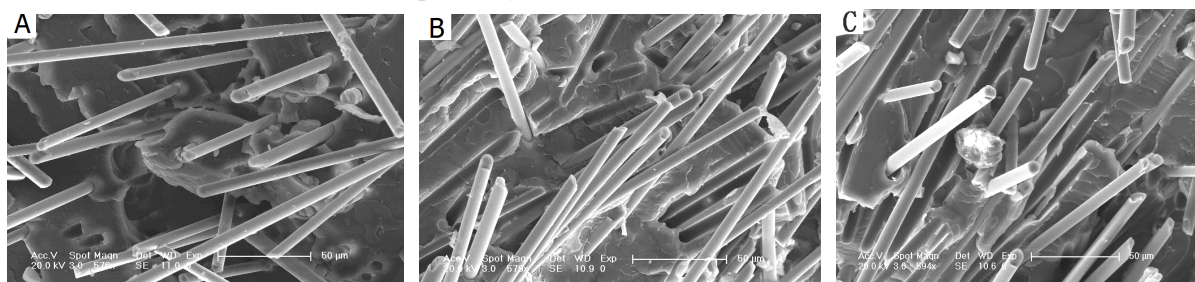


Fig.6 SEM micrographs of composites: without TAIC, non-irradiated: (A) PLA/BF 90/10 wt/wt; (B) PLA/BF 80/20 wt/wt; (C) PLA/BF 70/30 wt/wt.

The fracture surface morphology of enhanced irradiated samples is shown in Fig.7. Also the surfaces of pull-out fibers are smooth, but the holes left in the matrix are less obvious. And some deformation of PLA matrix during the tension process can be found from the fracture morphology, especially for the

sample irradiated at 70 kGy with the blending ratio of 70/30/5 wt/wt/wt. It is considered that a synergistic effect has been obtained between PLA matrix and filling fibers, and the interface adhesion is improved, which is resulted from the formation of the above-mentioned structure.

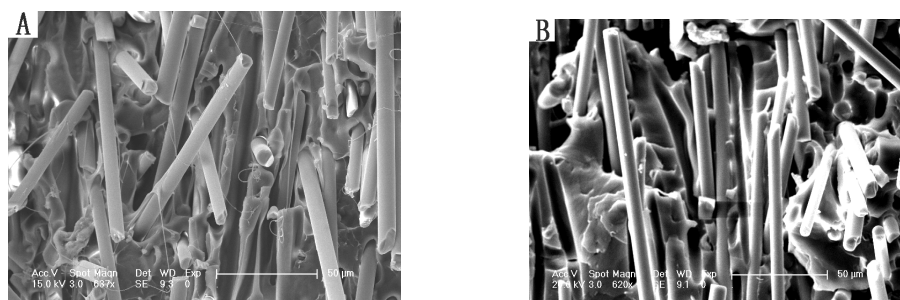


Fig.7 SEM micrographs of composites: (A) PLA/BF/TAIC 70/30/1 wt/wt/wt, 5 kGy; (B) PLA/BF/TAIC 70/30/5 wt/wt/wt, 70 kGy.

4 Conclusion

The introduction of basalt fiber and enhanced irradiation is an effective approach to improve the heat resistance of PLA. When 30wt% basalt fiber and 5wt% TAIC were employed, the HDT was dramatically enhanced to above 135°C after irradiation even at 5 kGy. Tensile strength of composites was improved by enhanced irradiation as well, and the optimum amounts of TAIC and absorbed dose were 5wt% and 70 kGy, respectively.

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